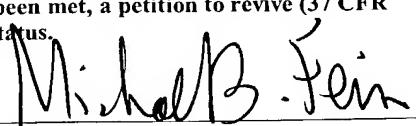


JC07 Rec'd PCT/PTO 19 DEC 2000

US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE FORM PCT/US/90 (REV 12-29-93)		ATTORNEY'S DOCKET NUMBER 119464
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/019161
INTERNATIONAL APPLICATION NO. PCT/FR00/01692	INTERNATIONAL FILING DATE 20 June 2000 (20-06-00)	PRIORITY DATE CLAIMED 21 June 1999 (21.06.99)
TITLE OF INVENTION HYDROPHOBIC CATIONIC DISPERSIONS STABILIZED BY MALEIMIDE COPOLYMERS OF LOW MOLECULAR MASS, FOR THE SIZING OF PAPER		
APPLICANT(S) FOR DO/EO/US BETREMIEUX Isabelle, DUMOUSSEAUX Christophe, VERGE Christophe, FERET Bruno, FLAT Jean-Jacques		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<ol style="list-style-type: none">1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))<ol style="list-style-type: none">a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))<ol style="list-style-type: none">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).b. <input checked="" type="checkbox"/> have been transmitted by the International Bureau.c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.d. <input type="checkbox"/> have not been made and will not be made.8. <input checked="" type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).		
Items 11. to 16. below concern document(s) or information included:		
<ol style="list-style-type: none">11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.14. <input type="checkbox"/> A substitute specification.15. <input type="checkbox"/> A change of power of attorney and/or address letter.16. <input checked="" type="checkbox"/> Other items or information:		
Translation of Amendments to claims under PCT Article 19 are enclosed as AMENDED SHEET pages 21 to 23. All of the claims are being amended via enclosed preliminary Amendment.		

U.S. APPLICATION NO. (if known) 10/01916	INTERNATIONAL APPLICATION NO. PCT/FR00/01692	ATTORNEY'S DOCKET NUMBER																
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$970.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$840.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00		CALCULATIONS PTO USE ONLY																
ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 840																		
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		\$																
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>- 20 =</td> <td>0</td> <td>X \$18.00</td> </tr> <tr> <td>Independent claims</td> <td>1 - 3 =</td> <td>0</td> <td>X \$78.00</td> </tr> <tr> <td colspan="2">MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td></td> <td>+ \$260.00</td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	- 20 =	0	X \$18.00	Independent claims	1 - 3 =	0	X \$78.00	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$260.00	\$
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TOTAL OF ABOVE CALCULATIONS = \$																		
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).		\$																
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property		\$																
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a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed.																		
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>501275</u> in the amount of <u>\$ 840</u> to cover the above fees. A duplicate copy of this sheet is enclosed.																		
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>501275</u> . A duplicate copy of this sheet is enclosed.																		
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.																		
SEND ALL CORRESPONDENCE TO Michael B. Fein Cozen O'Connor 1900 Market Street Philadelphia, PA 19103																		
 SIGNATURE Michael B. Fein NAME 25,333 REGISTRATION NUMBER																		

10/019161
531 Rec'd PCT 19 DEC 2001
Attorney Docket No. 11946

UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Isabelle **BETREMIEUX**

Christophe DUMOUSSEAUX

Christophe VERGE

Bruno FERET and

Jean-Jacques FLAT

FOR: : Hydrophobic Cationic Dispersions Stabilized by
Maleimide Copolymers of Low Molecular Mass,
for the Sizing of Paper

Serial No. : N/A

Filing Date : N/A

Attorney Docket : 119464

Assistant Commissioner for Patents
Washington, DC 20231

PRELIMINARY AMENDMENT

Prior to the Examination of the accompanying U.S. National Stage Application of PCT
Application PCT/FR00/01692 please amend as follows.

IN THE SPECIFICATION

Page 1, before line 4, insert as new line -- BACKGROUND OF THE INVENTION --

Page 5, before line 8, insert as new line -- SUMMARY OF THE INVENTION --

Page 6 before line 15, insert as new line -- DETAILED DESCRIPTION --

IN THE CLAIMS

Amend claims 1 to 11 and add claims 12 to 18 as set forth in the following Clean Copy of
Amended Claims.

CLEAN COPY OF AMENDED CLAIMS

1. Process for producing an aqueous cationic dispersion of polymers having hydrophobic characteristics comprising emulsion polymerizing at a temperature ranging from 30 to 100°C one or more monomers in the presence of 30 to 50% by weight, with respect to the one or more monomers, of a surfactant consisting of imidized styrene/maleic anhydride copolymer, the solids content of the dispersion being 20 to 50%.

2. Process according to claim 1 wherein the weight ratio of styrene to maleic anhydride of the copolymer is about 1/1 to 6/1.

3. Process according to claim 2 wherein the ratio is 2/1 to 4/1.

4. Process according to claim 1 wherein the copolymer has a number average molecular weight of about 500 to 20,000.

5. Process according to claim 4 wherein the number average molecular weight is 2000 to 5000.

6. Process according to claim 1 wherein the copolymer has a degree of imidization of about 50 to 100%.

7. Process according to claim 1 wherein the copolymer is imidized by dimethylpropylene diamine.

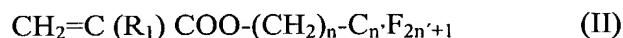
8. Process according to claim 1 wherein the monomer(s) are one or more of either (A) hydrophobic monomers selected from the group consisting of

(i) alkyl (meth)acrylates of the formula (I):



wherein $\text{R}_1 = \text{H}$ or CH_3 , and R_2 is a group having 1 to 22 carbon atoms;

(ii) perfluoroalkyl (meth)acrylates of formula (II):



wherein R_1 = H or CH_3 ; n = 1-4; and n' = 1-14;

- (iii) vinyl acetate;
- (iv) styrene; and
- (v) versatic esters; and

(B) hydrophilic monomers.

9. Process according to claim 8 wherein the monomer(s) comprise one or more hydrophobic monomers selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, and methyl methacrylate;

10. Process according to claim 8 wherein the monomer(s) comprise one or more relatively hydrophilic monomers selected from the group consisting of acrylic acid, methacrylic acid, acrylamide, and ethylene glycol (meth)acrylate.

11. Composition comprising an aqueous cationic dispersion prepared by process of claim 1.

12. Composition of claim 11 wherein the dispersed emulsion polymer particles have a size of about 50 to 500 nm.

13. Composition of claim 12 wherein the particle size is about 50 to 300 nm.

14. Composition of claim 11 wherein the dispensed emulsion polymer has a glass transition temperature of about -70°C to 100°C.

15. Composition of claim 11 wherein the glass transition temperature is about 0 to 50°C.

16. Process of treating paper or boards comprising using the composition of claim 11 as an internal sizing agent.

17. Process of claim 16 wherein no retention agent is used and immediate sizing is obtained.

18. Process of claim 16 wherein one or more additional sizing agents are used as surface sizing agents.

19. Process of claim 18 wherein the additional sizing agent(s) are selected from starches.

20. Composition useful for external sizing or internal sizing of paper or board comprising (A) an aqueous cationic dispersion prepared according to claim 1 and (B) starch in a weight ratio of (A) to (B) of about 5:95 to 50:50.

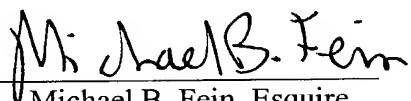
REMARKS

Claims 1 to 20 are in the case.

Claims 1 to 11 were presented in an amendment under Article 19 in the PCT Application from which the present application claims priority. The claims have all been rewritten to put them in a form more appropriate to U.S. practice. Each of the claims finds basis in the original claims and the specification.

Respectfully Submitted,

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PHILA1\1546864\5 099991 000

CLAIMS

1. Process for producing an aqueous cationic dispersion of polymers with a hydrophobic nature based on the emulsion polymerization at a temperature ranging from 30 to 100°C of at least one emulsion-polymerizable monomer in the presence of 30 to 50% by weight, with respect to the monomer(s), of an imidized styrene/maleic anhydride copolymer acting as sole surfactant, the solids content of the dispersion being from 20 to 50%.

2. Process according to Claim 1, characterized in that the styrene and the maleic anhydride of the said copolymer are taken in a ratio of 1/1 to 6/1 and preferably of 2/1 to 4/1.

3. Process according to Claim 1 or 2, characterized in that the said copolymer has a number-average molecular mass of between 500 and 20,000 and preferably between 2000 and 5000.

4. Process according to one of the preceding claims, characterized in that the degree of imidization of the said copolymer is between 50 and 100%.

5. Process according to one of the preceding claims, characterized in that the said copolymer is imidized by dimethylpropylenediamine.

6. Process according to any one of the preceding claims, characterized in that the monomer is chosen from the groups comprising:

- hydrophobic monomers, such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$, with $\text{R}_1=\text{H}$ or CH_3 and R_2 a group comprising 1 to 22 C,

perfluoroalkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COO}-(\text{CH}_2)_n-\text{C}_n\text{F}_{2n'+1}$, with $\text{R}_1=\text{H}$ or CH_3 , $n=1-4$ and $n'=1-14$,

vinyl acetate, styrene or versatic esters,

- relatively hydrophilic monomers, such as acrylic acid, methacrylic acid, acrylamide or ethylene glycol (meth)acrylate.

7. Cationic dispersion of polymers with a hydrophobic nature as can be had by the process of Claims 1 to 6, characterized in that the polymer particles have a size of between 50 and 500 nm and preferably of less than 300 nm.

8. Dispersion according to Claim 7, characterized in that the polymer with a hydrophobic nature has a glass transition temperature of between -70°C and 100°C and preferably between 0 and 50°C.

9. Use of the dispersion according to Claim 7 or 8 as internal sizing agent in the treatment of papers and boards.

10. Use of the dispersion according to Claim 7 or 8 in combination with other sizing agents, such as starch, in the surface sizing of papers and boards.

11. Composition for the external sizing of papers and boards comprising the dispersion according to either of Claims 7 and 8 and starch taken in a ratio by mass ranging from 5 to 50%.

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PCT/FR00/01692

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**HYDROPHOBIC CATIONIC DISPERSIONS STABILIZED
BY MALEIMIDE COPOLYMERS OF LOW MOLECULAR
MASS, FOR THE SIZING OF PAPER**

The present invention relates to the field of
5 the sizing of paper and in particular to sizing agents
based on an aqueous cationic dispersion of hydrophobic
polymers. It also relates to the process for producing
such dispersions.

A good sizing agent is desired for every kind
10 of paper, in particular printing and writing paper,
paper for labels, wastepaper and wrapping paper.

Two kinds of sizing agents generally exist:
surface or internal sizing agents. The term "surface
sizing agent" is understood to mean an agent applied at
15 the surface of papers, generally in conjunction with
starch, using a size press; on the other hand, the term
"internal sizing agent" is understood to mean an agent
added with the fibres in the wet part of the
manufacture of the paper.

20 A good surface sizing agent allows paper
manufacturers to obtain a paper with good resistance to
water while reducing and even sometimes eliminating
internal sizing, which requires a larger amount of
product than surface sizing. It also makes it possible
25 to obtain a paper with good surface properties, which
are particularly important in obtaining good
printability properties on papers.

It is now known to a person skilled in the art to use, as surface sizing agent, emulsified or dispersed polymers, in combination with starch, in preference to dissolved polymers. They make it possible 5 to obtain sizing agents having a high solids content with a low viscosity. They cause less of a foaming problem than dissolved polymers of the styrene-acrylic acid or styrene-maleic anhydride type, for example. These dispersions can be anionic or cationic, the 10 latter being less common and more difficult to synthesize.

As far as internal sizing agents are concerned, a person skilled in the art is looking for a product which can be used without a retention agent and 15 without a maturing stage. The commonest internal sizing agents are alkyl ketene dimer (AKD), alkyl succinic anhydrides (ASA) and colophonies. They are not suitable under all manufacturing conditions and with regard to all types of pulps and sometimes require the use of a 20 cationic promoter.

Surface sizing agents are known to a person skilled in the art and exist in the form of anionic dispersions. They are copiously described in the literature. They are synthesized by emulsion 25 polymerization using an anionic copolymer of low molecular mass as emulsifier. It is known to a person skilled in the art that the absence of surfactant

5 during the synthesis and a very fine particle size are preferable in obtaining satisfactory effectiveness during the surface treatment. Patent US 08,434,600 discloses, for example, the emulsion synthesis from
10 styrene-acrylic acid copolymers used without cosurfactant to give emulsions with a particle size of 65 nm, while Patent FR 9606737 claims the use of dispersions with a size of approximately 55 nm synthesized using styrene-maleic anhydride (SMA)
15 copolymers.

On the other hand, these anionic emulsions have certain disadvantages. In particular, they show little attachment to cellulose fibres which are slightly anionic, which causes recycling problems in
15 closed circuits. A high dosage is necessary in order to obtain good sizing properties, because a portion of the dispersion does not remain at the surface and spreads throughout the thickness of the paper sheet.
Furthermore, such anionic emulsions are not compatible
20 with some starches, such as, for example, cationic starches.

Cationic dispersions have therefore been envisaged as sizing agents. Several methods of synthesis are possible. That which proves to be the
25 most relevant and which the present invention relates to is emulsion polymerization using a cationic copolymer of low mass. Patent DE 2,454,397 claims the

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3 during the surface treatment. Patent US 08,434,600
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use of oligomers based mainly on styrene and on dimethylaminoethyl acrylate which are synthesized in an organic solvent. Patent DE 3,401,573 claims the use of styrene, acrylonitrile and dimethylaminoethyl acrylate 5 or methacrylate terpolymers. These two processes have the disadvantage of using an organic solvent which has to be removed before or after the emulsion polymerization. They are therefore neither economical nor ecological. Furthermore, there may be problems of 10 stability of the emulsion at high temperatures typical of sizing baths or at a high shear gradient. Another patent, DE 4,200,715, claims the use of a hydrophobic modified cationic polyamidoamine. This process results in emulsions with a very low solids content and with 15 particle sizes of about 160 nm. These emulsions are therefore neither economical nor effective in the present application.

According to the prior art, it therefore proves to be impossible to use, as sizing agent, 20 cationic emulsions which have a high solids content, which have a fine particle size and which are synthesized without organic solvent or surfactant.

United States Patent US 3,444,151 discloses, however, the synthesis of imide derivatives (II) of 25 copolymers based on maleic anhydride (I) and claims their use in emulsion polymerization for the purpose of latex synthesis. However, this patent claims the use of

compound (II) in a proportion of 2 to 20% by weight with respect to the monomers, which is in fact insufficient for the purpose of obtaining correctly stabilized latices in the absence of conventional surfactant (the examples taken up in the patent are, moreover, all based on the joint use of conventional surfactant).

The present invention provides a simple process for the synthesis of cationic emulsions and for 10 the application of these emulsions to paper, which give much better results than the equivalent anionic emulsions.

The present invention is distinguished from the prior art in that it uses cationic emulsions of a novel type which are intended to be used as sizing agent, which emulsions are obtained in the presence of imide derivatives (II) of copolymers based on maleic anhydride which are used in sufficient proportions to avoid recourse to conventional surfactants. The emulsions thus synthesized have high hydrophobicity, a fine particle size, a high solids content, weak foaming and good mechanical stability, good stability towards freezing/thawing and good stability at high temperatures. They can be used equally well as surface sizing agent and as internal sizing agent. In the surface application, they are compatible with a large number of starches. In the internal application, they

make possible immediate sizing without the use of a retention agent.

The invention therefore relates to the application, as sizing agents for papers, of cationic 5 dispersions resulting from the emulsion polymerization of a mixture of mainly hydrophobic monomers in the presence of an aqueous solution of imide derivatives of copolymers based on maleic anhydride of low molecular mass and in the absence of conventional surfactant. 10 Emulsion synthesis using these copolymers results in strongly hydrophobic cationic dispersions, with a high solids content and with a low particle size, which confer both very good hydrophobicity on the papers treated and good ink-jet printability.

15 One of the subject-matters of the invention is the aqueous dispersion of hydrophobic polymers which can be used alone or in combination with other agents as sizing agent for paper. It can be obtained according to the process described hereinbelow, which itself 20 constitutes another subject-matter of the invention.

The process for producing the aqueous dispersion used as sizing agent for papers is carried out by emulsion polymerization starting from an imide derivative (II) of a copolymer based on maleic anhydride. The synthesis of these derivatives, based on 25 the reaction of a diamine and of a polymer (I) based on maleic anhydride, is disclosed in Patent US 3,444,151.

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Briefly, these imide derivatives are obtained by reaction between a polymer (I) and a primary tertiary diamine, for example dimethylpropylenediamine (DMAPA), preferably by a bulk process. The primary amine 5 functional group will react with the anhydride functional group to form an amic acid and then this ring will reclose to form an imide derivative (II) of the polymer (I). The amine derivatives used in this invention are preferably those of the type I disclosed 10 in Patent US 3,444,151, that is to say those where a diamine reacts completely with the anhydride functional group with a molar ratio of 1 to 1. The use of copolymers exhibiting residual anhydride or acid 15 functional groups, resulting from a reaction with a deficiency of amine, is also possible.

The polymer (I) can be a copolymer or a terpolymer composed of maleic anhydride and of hydrophobic monomers chosen from α -olefins, unsaturated ethylenic aromatics, vinyl ethers or allyl ethers. The 20 preferred copolymer of the invention is a copolymer of styrene and of maleic anhydride (SMA) with a styrene to maleic anhydride ratio of 1/1 to 6/1, preferably of 2/1 to 4/1. The number-average molecular mass of the emulsifying copolymer is between 500 and 20,000, 25 preferably between 2000 and 5000. The percentage by mass of this oligomer in the final dry matter is between 10% and 40%, preferably between 20% and 30%.

The polymer (I) will preferably be chosen from copolymers of styrene and of maleic anhydride having acid numbers ranging from 500 to 200 mg KOH/g and sold by the company Elf Atochem under the names of 5 SMA® 1000, SMA® 2000, SMA® 3000, SMA® EF30, and SMA® EF40 and SMA® EF60.

After imidization, the copolymer is subsequently dissolved in aqueous solution and neutralized with an acid to give a cationic emulsifying 10 oligomer. The acid used will preferably be a volatile weak acid, such as ethanoic or methanoic acid.

The cationic emulsion is then synthesized, using conventional techniques for emulsion polymerization, in an aqueous solution comprising an 15 appropriate amount, preferably 30 to 50% with respect to the monomers, of the cationic emulsifier (II) described above and without addition of conventional macromolecular surfactant, in the presence of a conventional radical initiating system and of a mixture 20 of ethylenically unsaturated monomers, for example composed of styrene and of (meth)acrylic esters.

The radical initiator can be a water-soluble initiator, such as ammonium, potassium or sodium persulphates, optionally used in combination with a 25 reducing agent of sodium metabisulphite type, or alternatively hydrogen peroxide or a hydroperoxide, such as tert-butyl hydroperoxide, in combination with a

reducing agent, such as ascorbic acid or sodium formaldehydesulphoxylate. This initiator can also be soluble in organic media, such as azo derivatives, for example azobisisobutyronitrile, or organic peroxides.

5 The polymerization temperature is between 30°C and 100°C, preferably between 60°C and 90°C, and will be adjusted to the initiating system used.

10 The monomers are chosen in particular so as to obtain the desired glass transition temperature (Tg) but also the desired polarity, the desired functionality or the desired degree of cross-linking. This Tg can be between -70°C and 100°C, preferably between 0°C and 50°C.

15 By way of example, the monomers will be chosen from methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

CH₂=C(R₁)COOR₂, with R₁=H or CH₃ and R₂ a group comprising 1 to 22 C,

20 perfluoroalkyl (meth)acrylates of formula:

CH₂=C(R₁)COO-(CH₂)_n-C_{n'}F_{2n'+1}, with R₁=H or CH₃, n=1-4 and n'=1-14,

25 vinyl acetate, styrene, versatic esters, acrylic acid, methacrylic acid, acrylamide, ethylene glycol dimethacrylate, and the like.

The cationic dispersions of the invention have a solids content of between 20% and 50%,

preferably between 40% and 50%, and a particle size of between 50 nm and 300 nm with a mean particle size preferably of less than 100 nm. They have very good compatibility with the starches liable to be used in 5 the size press, even at high temperature, whether these are native starches, weakly anionic starches or cationic starches. They have a low viscosity, preferably of less than 100 mPa·s for a solids content of 41%. They have very good stability over time, very 10 good mechanical stability and very good resistance to the freezing/thawing cycle. They confer very good hydrophobicity on the papers treated, at treatment levels far below those of an equivalent anionic emulsion. In particular, they make possible the surface 15 treatment of papers of test liner type intended for board packing, where the papers are required to have very good hydrophobicity. They also make it possible to use, inter alia, a starch and pigments which are cationic during the surface treatment of the paper and 20 to obtain very good ink-jet printability. This is because the particles present in the printing inks are generally anionic and will attach more easily to the surface of the paper if cationic components are present.

25 Processes for the treatment of paper by external or internal sizing are described in the applicational examples.

Examples

The following examples illustrate the invention without limiting the scope thereof.

5 **Synthesis examples**

Example 1:

Synthesis of the cationic surface-active agent

This example describes the process for the 10 synthesis of an imide derivative of a styrene-maleic anhydride copolymer denoted by SMA.

Dimethylpropylenediamine (DMAPA) and then SMA are first of all introduced, at ambient temperature, into an electrically heated two-litre reactor equipped 15 with a stirring device suitable for viscous media. The reaction mixture is then heated to 150°C before starting the stirring and is then brought to 200°C. From this moment on, stationary conditions are maintained for 75 minutes before the imidized SMA is 20 extruded via the bottom valve of the reactor into a liquid nitrogen bath. The imidized SMA obtained is subsequently milled.

For Example S1-1, the reaction mixture comprises 170 g of DMAPA and 830 g of an SMA copolymer 25 composed of 79.8% by mass of styrene and 20.2% by mass of maleic anhydride with a number-average molecular

mass of 3000 (commercially available under the name of SMA® EF40 from Elf Atochem S.A.).

A powdered copolymer S1-1 is obtained, the characteristics of which are as follows:

5 Residual DMAPA = 600 ppm

Tg = 112°C

Acid number = 7.5 mg KOH/g.

Examples S1-2, S1-3 and S1-4

The same type of test can be carried out with
10 other copolymers of styrene and of maleic anhydride exhibiting other styrene/maleic anhydride ratios, the nature of the products employed, the amounts used and the final characteristics of the products obtained being summarized in the following table:

15

Reference	S1-2	S1-3	S1-4
SMA nature	SMA® 1000	SMA® 2000	SMA® 3000
Amount of SMA (g)	690	760	800
Amount of DMAPA (g)	310	240	200
Acid number (mg KOH/g)	7	2.6	10.6
Level of residual DMAPA (ppm)	600	600	600
Tg (°C)	82	80	91

Example 2:

Dissolution of the cationic surfactant (SUR)

171 g of the SUR S1-1, 644 g of water and 39 g of glacial acetic acid are introduced into a three-necked glass reactor with a capacity of 1 litre 5 equipped with a central stirrer, a condenser, a temperature probe and a device for introducing acetic acid. The combined reactants are heated to 60°C and kept stirring until the oligomer has completely dissolved.

10 The aqueous solution S2-1 obtained has an
S1-1 concentration of approximately 20%. The
dissolution of the SUR can optionally be carried out
directly in the polymerization reactor as a preliminary
stage of Example S3-1.

Example 3:

Synthesis of the cationic dispersion

This example describes the synthesis of a cationic dispersion according to the invention.

642 g of aqueous solution S2-1 comprising 20%
20 of oligomer S1-1 are introduced into a jacketed glass
reactor with a capacity of 1 litre equipped with a
central stirrer, a condenser, a temperature probe and a
device for continuously introducing an initiator
solution and a mixture or pre-emulsion of monomers, and
25 the reaction mixture is brought to 85°C.

Furthermore, an initiator solution is prepared by dissolving 3 g of ammonium persulphate in

60 g of demineralized water, and a mixture of monomers is prepared composed of 138 g of styrene and 162 g of butyl acrylate.

When the reaction mixture is at 85°C, the 5 initiator solution and the mixture of monomers are fed in over a period of 2 hours, with stirring and while maintaining the temperature at 85°C.

The reaction mixture is then kept stirring for an additional two hours at 85°C, then cooled to 10 ambient temperature, filtered through a 100 µm cloth and drained to result in the S3-1 dispersion, which exhibits the following characteristics.

Solids content = 41%

Viscosity is 35 mPa·s, measured using a 15 Brookfield device at 25°C according to the Standard

pH = 4

Mean diameter of the particles = 95 nm

Tg = 25°C

Comparative Example 1

20 A sizing agent is synthesized in the same way as that disclosed in Example 1 of Patent FR 9606737, to give an anionic emulsion S4 stabilized by a styrene-maleic anhydride copolymer neutralized with ammonia, composed of 74.3% by mass of styrene and 25.7% by mass 25 of maleic anhydride. This emulsion is therefore the anionic equivalent of the emulsion S3-1.

This emulsion S4 exhibits the following characteristics:

Solids content = 23.5%

Brookfield viscosity at 25°C = 20 mPa·s

5 pH = 8.85

Mean diameter of the particles = 55 nm

Tg = 25°C

Applicational examples

Three papers are surface treated using a
10 laboratory-scale size press.

The first two, of printing and writing type,
have a grammage of 80 g/m² and are sized with alkyl
ketene dimer (Aquapel® 315 from Hercules, hereinafter
AKD) at a level of 0.2% or 0.6% with respect to the
15 weight of the paper.

Another paper of the test liner type intended
to be used for the packing board application has a
grammage of 130 g/m² and was not subjected to any
internal sizing.

20 The following two tests were carried out in
order to measure the hydrophobicity and the resistance
to penetration by aqueous solutions of the papers
treated:

Cobb test: this test is well known to a
25 person skilled in the art and is described in
NF Standard EN 20535-ISO 535. The amount of water
absorbed after a given time is given in g/m². In this

instance, the Cobb test is carried out with a contact time of 60 seconds (Cobb₆₀) or of 30 minutes (Cobb₁₈₀₀).

HST test: this test is carried out according to Tappi Test Methods T Standard 530 OM-96. The papers to be tested have a size of 6 x 6 cm and are subjected, on one face, to a green ink (prepared with 1.25% of Naphthol Green B dye, 1% of formic acid and the remaining percentage of demineralized water). The penetration time of the aqueous ink is determined by reflection of a light source on the opposite face when the percentage of reflection reaches 80%.

Example A1

This example shows the advantage of the sizing agents according to the invention in the surface treatment of printing and writing papers with regard to their resistance to water and to penetration of the ink. An acceptable printing and writing paper must have a Cobb₆₀ of less than 30 and an HST of greater than 100.

The paper treated with 0.2% of AKD is surface sized with an aqueous solution comprising:

3% by weight of weakly anionic starch Amylis® 100 P (Roquette)

0.25% and 0.5% by weight of active material of the emulsions S3-1 and S4

The solution being brought to 100% by addition of the necessary complementary demineralized water.

The following results clearly show the superiority of the application according to the invention at a low treatment amount compared with the application using an anionic sizing agent:

5

Products	Starch alone	S3-1 0.25%	S3-1 0.5%	S4 0.25%	S4 0.5%
Cobb60 (g/m ²)	> 100	27.5	22.5	71	23
HST (s)	0	127	197	24	190

Example A2

This example shows the advantage of the sizing agents according to the invention in the surface treatment of printing and writing papers using a cationic starch. The latter introduces significant advantages with regard to the printability properties.

The papers treated with 0.2% and 0.6% of AKD are surface sized with a solution comprising:

15 3% by weight of cationic starch Catosize® 240
(National Starch)

0.5% by weight of active material of the emulsions S3-1 and S4

The solution being brought to 100% by
20 addition of the necessary complementary demineralized water.

The following results, in comparison with those of Example A1, clearly show the compatibility of the dispersion according to the invention with any type of starch. Whereas the properties of the emulsion S3-1 5 are reinforced in the presence of a cationic starch, those of the emulsion S4 decline and are even inferior to those of the starch alone for the paper with 0.6% of AKD, due to an incompatibility in the sizing slip.

10

Paper with 0.2% of AKD

Products	Starch alone	S3-1	S4
Cobb ₆₀ (g/m ²)	100	20.7	65
HST (s)	0	300	8

Paper with 0.6% of AKD

Products	Starch alone	S3-1	S4
Cobb ₆₀ (g/m ²)	52.5	19.5	59.5
HST (s)	9	120	7

15

Example A3

This example shows the advantage of the sizing agents according to the invention in the surface treatment of packing board papers, with regard to their 20 resistance to water. For these papers, very good

resistance to water is required over long periods of time. An acceptable paper of test liner type intended for packing board must have a Cobb1800 equal to or less than 120.

5 The paper of test liner type described above is surface sized with a solution comprising:

8% by weight of weakly anionic starch Amylis®
100 P (Roquette)

0.7% and 1.2% by weight of active material of
10 the emulsions S3-1 and S4

The solution being brought to 100% by addition of the necessary complementary demineralized water.

The following results demonstrate the
15 possibility of treating, with reasonable amounts of sizing agent according to the invention, papers of test liner type which have not been subjected to any internal sizing.

Products	Starch alone	S3-1 0.7%	S3-1 1.2%	S4 0.7%	S4 1.2%
Cobb60 (g/m ²)	200	30	20	61	28
Cobb1800 (g/m ²)	250	150	105	165	150

Example A4

This example describes the use of the cationic dispersion of the invention as internal sizing agent.

5 The paper is obtained according to the process which consists in preparing handsheets on a Franck device starting from a pulp beaten to a certain Schopper-Riegler degree of drainability (see NF Standard Q 50003). The sizing agent is added to the
 10 fibrous suspension composed of 5 g/l of fibres in water. Stirring is continued for 3 minutes. The handsheet is prepared at a mean grammage of 65 g/m², after draining, dewatering and drying for 5 minutes at 95°C. The pulp used in this instance is composed of 50%
 15 short fibres and 50% long fibres and has a Schopper-Riegler degree of 25.

1% of sizing agent with respect to the dry fibrous matter is added. The sizing agents used are emulsions S3-1 and S4, as well as AKD (Aquapel® 315
 20 from Hercules). The handsheets treated with AKD are subjected to accelerated maturing in an oven for 10 minutes at 110°C.

Sizing agent	None	AKD	S3-1	S4
Cobb ₆₀	> 100	42	24	> 100

As is seen in the light of these results, the emulsion S3-1 gives entirely satisfactory sizing results without a retention agent, whereas the performance is mediocre with AKD used alone.

5 Furthermore, no maturing stage is necessary. The anionic emulsion does not give any result because it is not attached to the fibres.

CLAIMS

1. Process for producing an aqueous cationic dispersion of polymers with a hydrophobic nature based on the emulsion polymerization at a 5 temperature ranging from 30 to 100°C of at least one emulsion-polymerizable monomer in the presence of 20 to 60% by weight, with respect to the monomer(s), of an imidized styrene/maleic anhydride copolymer acting as sole surfactant, the solids content of the dispersion 10 being from 20 to 50%.

2. Process according to Claim 1, characterized in that the styrene and the maleic anhydride are taken in a ratio of 1/1 to 6/1 and preferably of 2/1 to 4/1.

15 3. Process according to Claim 1 or 2, characterized in that the said copolymer has a number-average molecular mass of between 500 and 20,000 and preferably between 2000 and 5000.

20 4. Process according to one of the preceding claims, characterized in that the degree of imidization of the said copolymer is between 50 and 100%.

25 5. Process according to one of the preceding claims, characterized in that the said copolymer is imidized by dimethylpropylenediamine.

6. Process according to any one of the preceding claims, characterized in that the monomer is chosen from the groups comprising:

- hydrophobic monomers, such as methyl 5 acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate and more generally alkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COOR}_2$, with $\text{R}_1=\text{H}$ or CH_3 and R_2 a group comprising 1 to 22 C,

10 perfluoroalkyl (meth)acrylates of formula:

$\text{CH}_2=\text{C}(\text{R}_1)\text{COO}-(\text{CH}_2)_n-\text{C}_{n'}\text{F}_{2n'+1}$, with $\text{R}_1=\text{H}$ or CH_3 , $n=1-4$ and $n'=1-14$,

vinyl acetate, styrene or versatic esters,

- relatively hydrophilic monomers, such as 15 acrylic acid, methacrylic acid, acrylamide or ethylene glycol (meth)acrylate.

7. Cationic dispersion of polymers with a hydrophobic nature as can be had by the process of Claims 1 to 6, characterized in that the polymer 20 particles have a size of between 50 and 500 nm and preferably of less than 300 nm.

8. Dispersion according to Claim 7, characterized in that the polymer with a hydrophobic nature has a glass transition temperature of between 25 -70°C and 100°C and preferably between 0 and 50°C .

9. Use of the dispersion according to Claim 7 or 8 as internal sizing agent in the treatment of papers and boards.

10. Use of the dispersion according to Claim 5 7 or 8 in combination with other sizing agents, such as starch, in the surface sizing of papers and boards.

11. Composition for the external sizing of papers and boards comprising the dispersion according to either of Claims 7 and 8 and starch taken in a ratio 10 by mass ranging from 5 to 50%.

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**(54) Title: HYDROPHOBIC CATIONIC DISPERSIONS STABILISED BY LOW MOLECULAR WEIGHT MALEIMIDE
COPOLYMERS, FOR PAPER SIZING**

**(54) Titre: DISPERSIONS CATIONIQUES HYDROPHOBES STABILISEES PAR DES COPOLYMERES MALEIMIDES DE
FAIBLE MASSE MOLECULAIRE, POUR LE COLLAGE DU PAPIER**

(57) Abstract: The invention concerns a method for obtaining an aqueous dispersion of hydrophobic polymers dispersed in the form of particles with mean diameter less than 100 nm stabilised solely with a macromolecular surfactant based on low molecular weight styrene/maleic anhydride imide copolymer. The invention also concerns the use of said dispersion for treating and sizing paper.

(57) Abrégé: L'invention décrit un procédé nouveau pour l'obtention d'une dispersion aqueuse de polymères hydrophobes dispersés sous la forme de particules de diamètre moyen inférieur à 100 nm stabilisées uniquement par un tensio-actif macromoléculaire à base de copolymère styrène / anhydride maleique imidisé de faible masse. L'invention décrit aussi l'utilisation d'une telle dispersion dans le traitement et le collage du papier.

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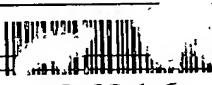
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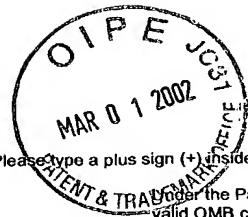
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